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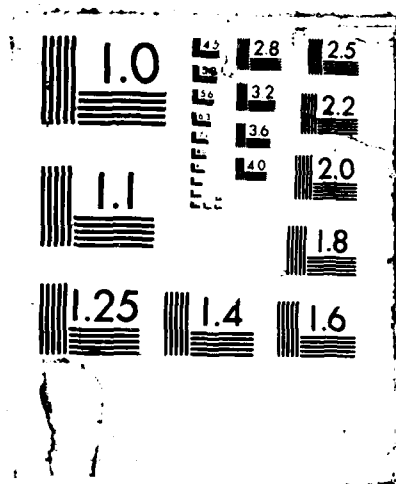
MEASUREMENT OF RATE CONSTANTS OF ELEMENTARY GAS
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OF CHEMISTRY M F GOLDE 31 OCT 87 AFOSR-TR-87-1725
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ABSTRACT

Important elementary gas-phase reactions have been studied by the discharge-flow technique, utilizing laser-induced fluorescence to detect radical species and mass spectrometry to monitor stable reaction products. Both rate constants and reaction products have been determined. The H-abstraction reactions of F atoms and of OH radicals with CH_3OH favor different reaction channels: the former yields predominantly methoxy radicals (CH_3O), whereas the latter strongly favors hydroxymethyl (CH_2OH). The reaction of OH with CH_3OH shows a large kinetic isotope effect for this channel.

The kinetics of CH_3O with NO resemble those of CH_3O with NO_2 studied previously in this lab, namely a weak positive pressure dependence and a strong inverse temperature dependence of the second order rate coefficient. Analysis of the rate data together with direct detection of reaction products have established that atom transfer to yield $\text{HNO} + \text{CH}_2\text{O}$ is the major channel at low pressures.

A brief study of the reaction of NH_2 with NO has shown that OH production is a minor channel, with a branching fraction of < 0.04 .

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A. Introduction

This project commenced in March 1985, with plans to explore a range of elementary reactions on three separate pieces of equipment. After the death of the principal investigator, Professor Kaufman, in July 1985, it was decided to consolidate the investigation onto a single apparatus, which is described in the next section. A few other significant results were obtained on a separate flow system.

The grant period was reduced from the original three years to two years, but subsequently allowed a 6-month no-cost extension. During this period, the personnel involved in the project were Dr. Stuart Anderson (until November 1985), Dr. Joseph Durant (until February 1987), and three graduate students, two of whom have graduated, Nicola Mendoza (M.S.) and James McCaulley (Ph.D.).

The projects completed include: investigation of the products of the $F + CH_3OH$ reaction; measurement of the room temperature rate constant of the reaction $OH + CH_3OH$ and several isotopic analogs; measurement of rate constants and product channels in the reaction $CH_3O + NO$; and a brief investigation of the yield of OH in the reaction of NH_2 with NO . A further study of $CH_3O + O$ was underway at the completion of the project.

In each case, valuable information has been obtained concerning the reaction products: for the reactions $F + CH_3OH$ and $NH_2 + NO$, the products were detected directly; for $OH + CH_3OH$, the information was provided by the observed kinetic isotope effects; and for $CH_3O + NO$, in addition to direct product measurements, valuable insight was provided by the observed pressure dependence of the rate coefficient.

B. Experimental

Most experiments were carried out using a 1-inch i.d. flow tube reactor,

equipped with mass spec and LIF detection techniques, which has been described previously.^{1,2} Radicals were prepared initially using IR multi-photon dissociation of suitable precursor species. This is accompanied, however, by production of unwanted side-products and it was decided to adopt a more-traditional microwave discharge source, utilizing gas-phase titration reactions downstream to create the radical of interest. The other reagent was added through a movable inlet, allowing reaction distances of 5-50 cm, corresponding to reaction times up to ~ 0.1 sec. For laser-induced fluorescence measurements, an excimer pumped dye laser (Lambda-Physik EMG103 MSC, FL 2001) was used; the output is characterized by a bandwidth of ~ 0.3 cm^{-1} , a pulse duration of ~ 15 ns, and a maximum pulse energy of ~ 0.1 mJ at 300 nm. A repetition rate of 48.5 Hz was employed in most experiments. The pulse energy was monitored continuously with a photodiode (EG&G FND-100Q). The fluorescence was collected with lenses (f/2.4) and detected by a filtered photomultiplier (EMI 9813QB or 9789QB), used in the pulse-counting mode. The signal was processed by an amplifier-discriminator (EG&G 1182 or Pacific Instruments AD6) and a gated counter (Tennelec TC535P). The signal was transferred to a lab. computer (HP 9816), where corrections for drift in laser pulse energy could be applied. Where necessary, with large fluorescence signals, the excimer laser output was attenuated, and the signal gate delayed several microseconds with respect to the laser pulse to prevent pulse pile-up errors.

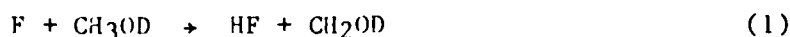
At the downstream end of the flow tube, the gas was sampled by a 1.0 mm id stainless steel orifice into the differentially-pumped mass spectrometer chamber. A second orifice (0.9 mm id) collimates the beam before it enters the crossed-axis electron-impact ion source and quadrupole mass filter (Extrel, 7-162-8 with ELFS). The transmitted ions are detected with a focussed mesh electron multiplier (Johnston Labs., MM-1), mounted off-axis to the mass filter.

In the first chamber, the molecular beam can be modulated by a tuning-fork chopper, allowing phase-sensitive detection of the output signal. The detection limit of the mass spectrometer is $\sim 5 \times 10^9 \text{ cm}^{-3}$ for stable molecules.

C. Results and Discussion

1. Product Channels of the Reaction $\text{F} + \text{CH}_3\text{OH}$.

This fast reaction ($k = 2 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$) was examined as a potential source of CH_3O radicals for kinetic studies. F atoms were generated by discharging a dilute mixture of F_2 in Ar or He. Careful tests showed that the F_2 dissociation efficiency was close to unity under the conditions used. Sufficient CH_3OD or CD_3OH was added downstream to drive the reaction rapidly to completion, and the relative yields of HF and DF products were determined using mass spectrometry at $m/e = 20$ and 21 respectively.

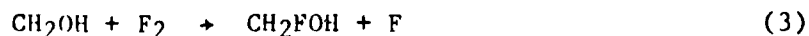


The measured branching fractions for CH_3O formation are 0.81 ± 0.07 and 0.69 ± 0.08 for reaction of CH_3OD and CD_3OH respectively. Measurements were made over a concentration ratio range, $[\text{methanol}]/[\text{F}]$ of 2 to 80, a total carrier gas pressure of 0.5 - 2 Torr, and with both uncoated and wax-coated flow tubes.

Literature values of the branching fraction are listed in Table 1; they range from 0.3 to 0.6. The study of Hoyermann et al³ is the most similar in concept; however, they found the HF and DF mass spec. signals to be very irreproducible and their branching fractions for methoxy formation have very large uncertainties, 0.3 ± 0.1 for reaction with CH_3OD and 0.5 ± 0.2 for CD_3OH . The other studies are either less direct or require assumptions in order to extract branching fractions. We conclude that the branching fraction is still

uncertain, and further experiments are warranted to distinguish between the higher value, 0.7 - 0.8, obtained in the present study, and the lower values, 0.3 - 0.5, reported by others.

It has been reported⁴ that addition of F₂ to the reaction products enhances the CH₃O yield via the reaction sequence:



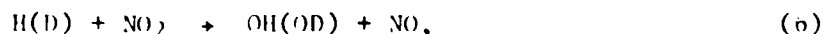
and leads to quantitative conversion of CH₂OH to CH₃O. We found that addition of F₂ downstream of the F + CH₃OD reaction zone caused large increases in the HF and DF yields, much beyond those expected, even if decomposition of an activated CH₂FOD intermediate:



is postulated. This implies that the F₂-initiated reaction sequence is complex and is thus not recommended as a clean source of CH₃O.

2. Investigation of the Reaction OH + CH₃OH.

This study was commenced in order to probe potential CH₃O-producing side-reactions in the planned investigation of the reaction CH₃O + O. Rate coefficients were measured at room temperature for reactions of seven isotopically-distinct sets of reagents. OH (OD) was produced by the fast reaction



and was monitored by LIF at ~308 nm. Decay plots of ln (I_{LIF}) vs reaction distance were linear in most instances and the derived first order rate

coefficients were plotted against the methanol concentration to obtain the second order rate constants. Careful analysis showed that possible removal of OH by secondary processes:



should be slight under the conditions used. These processes would lead to an overestimation of the rate constant of interest by <15%.

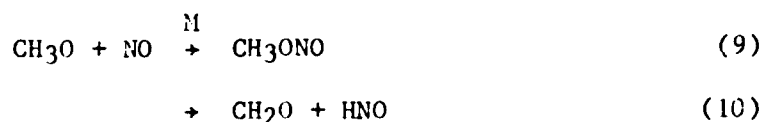
The rate constants are listed in Table 2. The value for OH + CH₃OH is in good agreement with five previous studies,⁵⁻⁹ which yielded values of between 7.6 and 10.6 x 10⁻¹³ cm³s⁻¹. The rate constant at 300K appears to be well established. The current study appears to be the first of isotopic variants of the title reaction. It is clear (see Table 2) that substitution of D for H at the CH₃ group has a much larger effect on the rate constant than that at the OH groups. It is generally accepted that the largest isotope effects are seen at the bond broken during the atom-transfer reaction (primary isotope effect). This implies that C-H cleavage is favored over O-H cleavage in the reaction. If it is assumed that reaction occurs independently at each site (i.e. no secondary isotope effect), then it can be deduced that the branching fraction for formation of CH₃O + H₂O is $f = 0.21 \pm 0.09$ in the OH + CH₃OH reaction. For removal of an H or D atom from the methyl group, the mean value of f corresponds to a kinetic isotope effect, $k_H/k_D \sim 9.0$. The branching fraction is consistent with previous measured values of 0.11, 0.17 and 0.25,^{5,6} but unfortunately does not significantly decrease the uncertainty in this quantity.

The contrast in branching fractions in the reaction of F and OH with CH₃OH can be understood in terms of the energetics of the reactions. The HF bond energy is 5.9 eV, so that both channels are strongly exothermic. However, the

H-OH bond energy is only 5.1 eV, and the exothermicities of the two channels are now significantly different, 1.1 eV for formation of $\text{CH}_2\text{OH} + \text{H}_2\text{O}$, but only 0.6 eV for formation of $\text{CH}_3\text{O} + \text{H}_2\text{O}$. This is reflected in the significantly larger activation energy, which has been measured for the latter channel.

3. Investigation of the reaction $\text{CH}_3\text{O} + \text{NO}$.

This reaction is of possible importance in polluted atmospheres and is of direct relevance to the decomposition of CH_3ONO , a model propellant. The reaction is of interest as it offers the possibility of two competing channels:



The latter channel may occur via two possible mechanisms: either direct abstraction of H from CH_3O , or unimolecular decomposition of the intermediate CH_3ONO . We have measured the second-order rate constant of the overall reaction over the pressure range ($\text{M} = \text{He}, \text{Ar}$) 0.75 - 5 Torr and the temperature range 223 - 473K. The reaction products have been examined over a smaller range of conditions. For the kinetic measurements, CH_3O radicals were produced by two separate reactions:

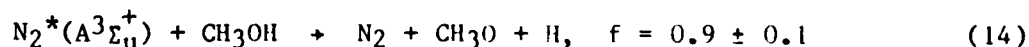


In each case, F atoms were produced by discharging a dilute mixture of F_2 in He. CH_3O was detected by LIF in the ($\text{A}^2\text{A}_1 - \text{X}^2\text{E}$) band system, utilizing lines in the 3^2_0 band at 303.8 nm. Initial concentrations of CH_3O in the reaction zone were typically $< 5 \times 10^{11} \text{ cm}^{-3}$.

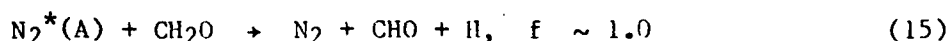
In the presence of NO, CH₃O decayed exponentially over a concentration range of at least 10, but often flattened out at large reaction times, indicative of a secondary process forming CH₃O radicals. The source was not definitely identified, but heterogeneous processes are suspected. Kinetic data were derived from the linear portions of the plots of $\ln(I_{LIF})$ vs reaction time. Typical decay curves are shown in Fig. 1, and a plot of the first order rate coefficient vs [NO] in Fig. 2. The slope yielded the second-order rate coefficient, which is listed with the other data from this study in Table 3. The rate coefficient increases slightly with pressure between 1 and 5 Torr, and decreases significantly with increasing temperature between 200 and 450K, as illustrated in Fig. 3.

The products of this reaction were investigated in two ways. CH₃ONO was detected via mass spectrometry at m/e 61 (parent) and 60. The signal was calibrated using pure CH₃ONO. A small correction was applied for CH₃NO₂, detected as a minor product of the CH₃ + NO₂ precursor reaction, equ. 12. [It was concluded that the branching fraction for CH₃NO₂ formation was 0.040 ± 0.004 at 0.5 Torr total pressure, and 0.07 ± 0.02 at 1 Torr]. For the CH₃O + NO reaction, the branching fractions for CH₃ONO formation were 0.11 ± 0.02 (0.52 Torr, 298K), 0.20 ± 0.05 (1.0 Torr, 298K) and 0.16 ± 0.05 (1.0 Torr, 223K).

A brief search for HNO, a product of the other channel of this reaction, equ. 10, was not successful in this apparatus. Therefore, the reaction was studied in another flow system, with CH₃O formed by the reaction:¹⁰



HNO was readily detected via LIF in the ($A^1A'' - X^1A'$) band system. The signal was compared with that from the reaction sequence:



This study confirmed that the yield of HNO in reaction (9,10) is large at low pressures. Quantitative comparison with the CH_3ONO measurements awaits characterization of possible wall loss of CHO and CH_3O between the $\text{N}_2(\text{A})$ and NO inlet points.

The measured rate constants agree well with those of a previous study,¹¹ which spanned the pressure range 3 - 190 Torr. Deconvolution of the rate data of Table 3 to yield rate constants for the recombination (k_{rec}) and atom transfer (k_{AT}) channels (equ. 9 and 10 respectively) is hampered by the fact that the combination channel cannot be assumed to be exhibiting limiting low pressure behavior even at the low pressures of this study. According to Lindemann-Hinshelwood theory, the effective second order rate coefficient, k^{II} , for this channel can be determined, given the limiting low pressure (k_0^{III}) and high pressure (k_∞^{II}) rate constants.

$$k_{\text{rec}}^{\text{II}} = k_0^{\text{III}} k_\infty^{\text{II}} [\text{M}] / (k_0^{\text{III}} [\text{M}] + k_\infty^{\text{II}}) = k_{\text{LH}}, \quad (17)$$

where M is the buffer gas (Ar or He). However, this theory is oversimple and Troe¹² has suggested an amended expression which yields good agreement, for the fall-off behavior, with RRKM theory. This approach is attractive as, apart from k_∞ , the model essentially contains only one variable parameter, S_K , which can be readily estimated from the known fundamental vibration frequencies of CH_3ONO .

Using the measured high pressure rate constant,¹¹ $1.2 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$, for k_∞^{II} and applying this model, values of the rate constants for the two channels were determined by a least squares fit to the rate coefficients at room temperature: $k_{\text{AT}} = (2.89 \pm 0.07) \times 10^{-12} \text{ cm}^3\text{s}^{-1}$, and $k_{\text{rec},0}^{\text{III}} = (2.9 \pm 0.3) \times 10^{-29} \text{ cm}^6\text{s}^{-1}$. In

the absence of experimental information, k_{∞}^{II} was assumed to be independent of temperature and $k_{\text{O}}^{\text{III}}$ to vary as T^{-n} . A least squares fit to the complete set of rate data (223 - 473K) yielded $n \sim -2.5 \pm 1.0$. Thus, within the limits of the assumption concerning k_{∞}^{II} , the following rate constants were derived:

$$k_{\text{rec},0}^{\text{III}} = (2.9 \pm 0.3) \times 10^{-29} (T/300)^{-2.5 \pm 1.0} \text{ cm}^6\text{s}^{-1} \quad (18)$$

$$k_{\text{AT}} = (7.9 \pm 1.0) \times 10^{-13} e^{(400 \pm 40)/T} \text{ cm}^3\text{s}^{-1}. \quad (19)$$

These predict branching fractions for the recombination channel of 0.10 ± 0.02 (297K, 0.5 Torr), 0.17 ± 0.02 (297K, 1.0 Torr) and 0.23 ± 0.06 (223K, 1.0 Torr), in fair agreement with the measured yields of CH_3ONO . At 4.0 Torr and 297K, the predicted HNO branching fraction is 0.65 ± 0.10 , in moderate agreement with the uncorrected preliminary value of 0.3 - 0.4.

Previous studies have failed to establish the product distribution principally because CH_3ONO has been employed as the source of CH_3O . For instance, Sanders et al.¹³ observed the kinetics of HNO formation to match those of CH_3O removal, whereas Zellner,¹¹ in a similar experiment, observed CH_2O formation to be limited to the photolysis pulse duration. Thus, while both studies observed $\text{HNO} + \text{CH}_2\text{O}$ formation, the former group ascribed it to a channel of the $\text{CH}_3\text{O} + \text{NO}$ reaction, but Zellner ascribed it to a channel of CH_3ONO photodissociation. Other investigations^{14,15} employed steady-state photolysis or thermal dissociation of CH_3ONO and are less direct; however, these found a small branching fraction of 0.10 - 0.15 for reaction (10) at high pressures.

The present study has demonstrated clearly that atom transfer is the major channel at low pressure. The inverse temperature dependence for this channel (which is evident from Fig. 3 and is independent of the way in which the recombination channel is modeled) suggests strongly that this channel occurs

mainly via decomposition of the energetic CH_3ONO intermediate rather than via direct abstraction of a H atom. Thus, the rate coefficient for this channel should become smaller at high pressure, because of competitive collisional stabilization of the intermediate. Our findings are qualitatively in agreement with previous studies. A more quantitative comparison could be achieved by RRKM calculations which, however, require considerable information concerning the potential energy surface for this reaction.

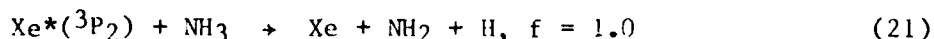
4. Study of the reaction $\text{NH}_2 + \text{NO}$.

This reaction has been the subject of many experimental investigations. Controversy concerns both the rate constant and the products, detection of OH in the absence of H atoms providing evidence for the channel:

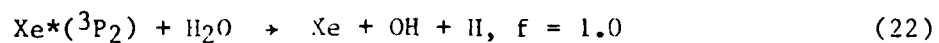


In a recent summary of data,¹⁶ the OH branching fraction spanned the range <0.13 to >0.65 .

A 'conventional' study of this reaction in this lab with $\text{F} + \text{NH}_3$ as the source of NH_2 gave irreproducible results and clear evidence of the importance of secondary reactions, including wall processes. In an attempt to reduce these complications, the reaction was then studied in a separate apparatus, using the extremely fast formation reaction:



The system was tested by measuring the rate constant of the overall $\text{NH}_2 + \text{NO}$ reaction, with NH_2 monitored by LIF. The value obtained, $1.40 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$, is well within the range of previous measurements. The small OH yield from the reaction was compared with that from the reaction:



In this case, it proved possible to correct for wall loss of NH_2 between the NH_3 and NO inlets. A branching fraction for OH production in the $\text{NH}_2 + \text{NO}$ reaction of 0.04 was obtained. It is thus concluded that the channel leading to $\text{OH} + \text{N}_2\text{H}$ is very minor and that the large yields of OH seen in previous studies arise principally from secondary reactions.

Table 1
Branching in the Reaction of F with CH₃OH

| Reagent | Method | f _{CH₃O(CD₃O)} | Reference |
|--------------------|-------------------------------|---|-----------|
| CH ₃ OD | HF,DF IRCL | 0.50 | a |
| CH ₃ OD | HF,DF IRCL | 0.31 ± 0.03 | b |
| CH ₃ OD | HF,DF mass spec. | 0.3 ± 0.1 | c |
| CD ₃ OH | HF,DF mass spec. | 0.5 ± 0.2 | c |
| CH ₃ OH | CH ₂ OH mass spec. | 0.59 ± 0.06 | d |
| CH ₃ OD | HF,DF IRCL | 0.38 ± 0.24 | e |
| CD ₃ OH | HF,DF IRCL | 0.63 ± 0.15 | e |
| CH ₃ OD | HF,DF mass spec. | 0.81 ± 0.07 | this work |
| CD ₃ OH | HF,DF mass spec. | 0.69 ± 0.08 | this work |

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- d. V. Meier, H. H. Grotheer and Th. Just, Chem. Phys. Lett. 106 97 (1984).
- e. M. A. Wickramaaratchi, D. W. Setser, H. Hildebrandt, B. Korbitzer and H. Heydtmann, Chem. Phys. 95 109 (1985).

Table 2

Hydroxyl + Methanol: Second-order Rate Coefficients.

 $T = 298 \pm 2\text{K}$; $p = 3.00 \pm 0.05$ Torr.

| Reaction | # of methanol concentrations | $10^{13}k_{\text{II}}, \text{cm}^3\text{s}^{-1}$ |
|-------------------------|------------------------------|--|
| OH + CH ₃ OH | 14 | 10.1 ± 1.0 |
| OD + CH ₃ OH | 8 | 9.5 ± 1.2 |
| OD + CH ₃ OD | 8 | 9.3 ± 1.1 |
| OH + CD ₃ OH | 14 | 3.35 ± 0.72 |
| OD + CD ₃ OH | 8 | 2.86 ± 0.37 |
| OH + CD ₃ OD | 33 | 1.93 ± 0.45 |
| OD + CD ₃ OD | 20 | 1.67 ± 0.16 |

Table 3

CH₃O + NO: second-order rate coefficients.

| T, K | p, torr | # ^a | 10 ¹² k _{II} , cm ³ s ⁻¹ |
|------|-------------------|----------------|--|
| 223 | 1.05 | 6 | 6.46 ± 0.84 |
| " | 2.04 | 7 | 7.4 ± 1.0 |
| " | 3.01 | 5 | 7.92 ± 0.96 |
| " | 5.04 | 9 | 7.8 ± 1.7 |
| 260 | 1.01 | 7 | 3.99 ± 0.50 |
| " | 2.99 | 6 | 5.13 ± 0.63 |
| " | 5.01 | 7 | 7.76 ± 0.92 |
| 297 | 0.71 | 8 | 3.14 ± 0.45 |
| " | 0.72 ^b | 8 | 3.61 ± 0.54 |
| " | 0.74 | 4 | 3.97 ± 0.47 |
| " | 0.85 | 7 | 3.97 ± 0.57 |
| " | 1.05 | 7 | 3.78 ± 0.69 |
| " | 1.52 ^b | 7 | 4.33 ± 0.73 |
| " | 1.57 | 6 | 4.27 ± 0.75 |
| " | 1.75 | 5 | 4.19 ± 0.60 |
| " | 2.05 | 6 | 3.68 ± 0.49 |
| " | 3.04 | 6 | 5.00 ± 0.73 |
| " | 3.88 | 5 | 4.54 ± 0.54 |
| " | 3.89 ^b | 7 | 4.07 ± 0.61 |
| " | 4.03 | 7 | 4.46 ± 0.67 |
| " | 5.07 | 7 | 4.98 ± 0.57 |
| 345 | 1.07 | 8 | 2.78 ± 0.41 |
| " | 5.06 | 10 | 4.06 ± 0.57 |
| 396 | 1.07 | 4 | 2.60 ± 0.35 |
| " | 5.06 | 6 | 3.29 ± 0.57 |
| 423 | 1.07 | 6 | 2.03 ± 0.32 |
| " | 5.06 | 6 | 2.50 ± 0.49 |
| 473 | 1.45 | 5 | 2.34 ± 0.37 |
| " | 5.09 | 4 | 2.32 ± 0.42 |

a. number of NO concentrations

b. M = Ar

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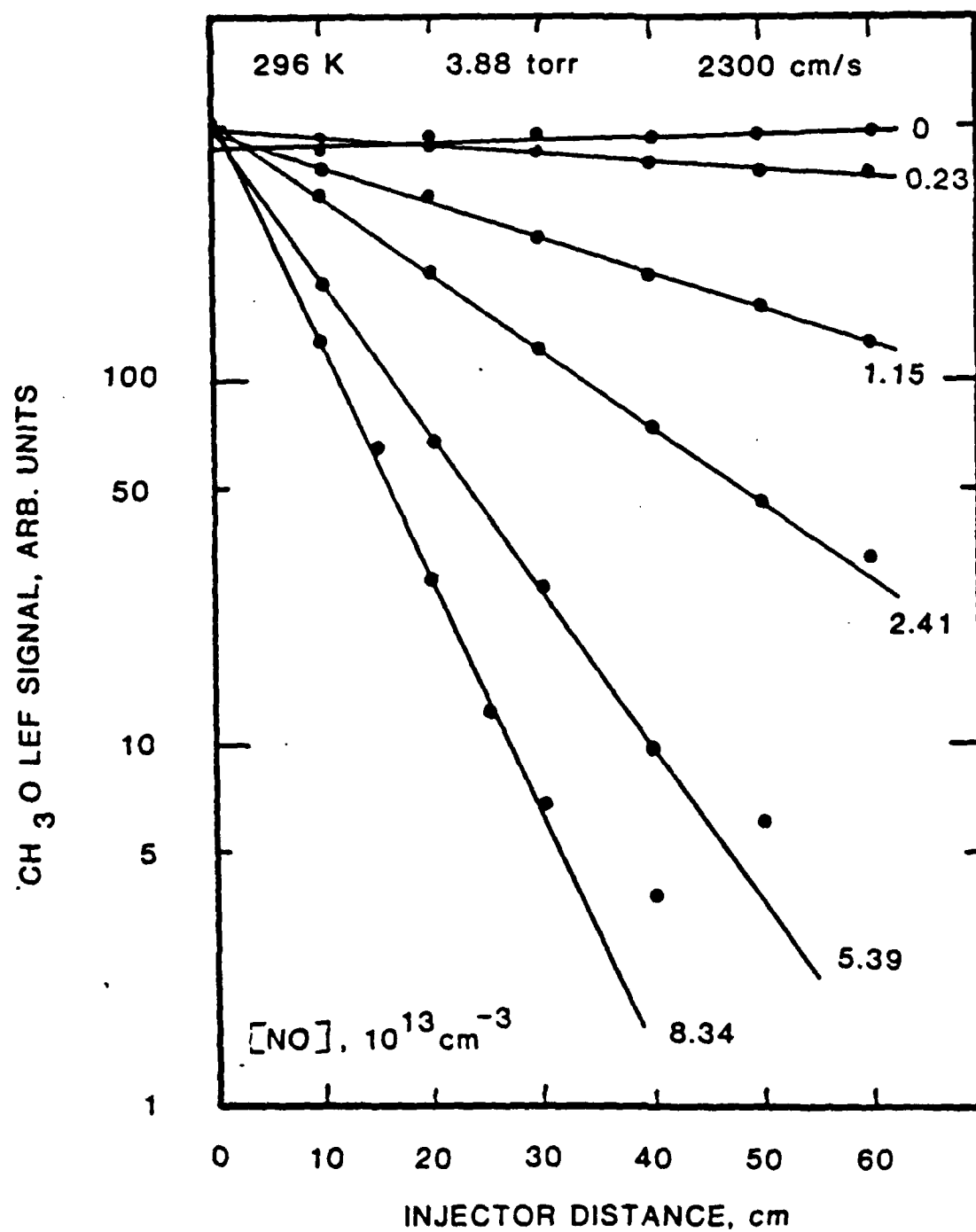


Figure 1. CH₃O + NO: decay plots with curvature attributed to CH₃O self-reaction

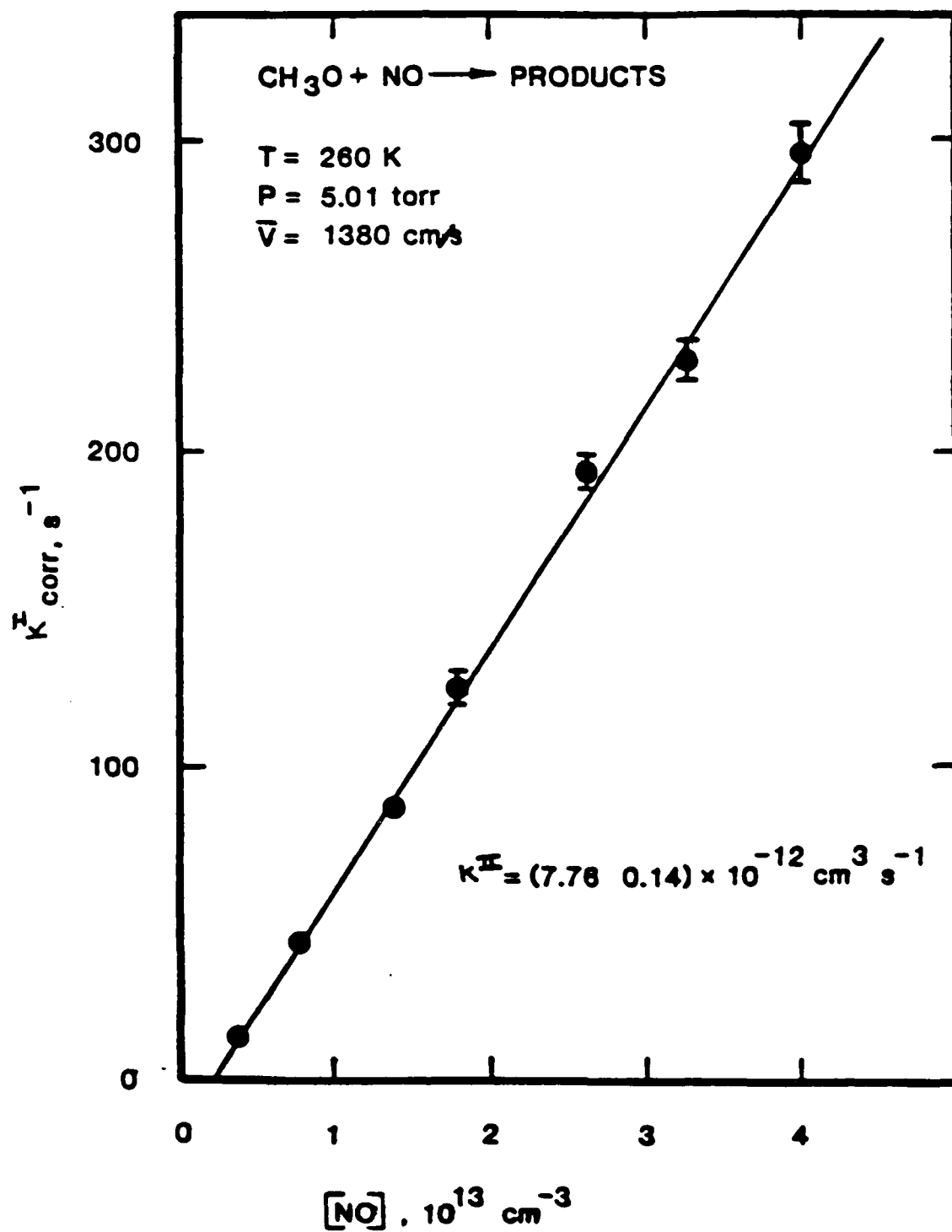


Figure 2. CH₃O + NO: $k^{\text{II}}_{\text{corr}}$ vs [NO]

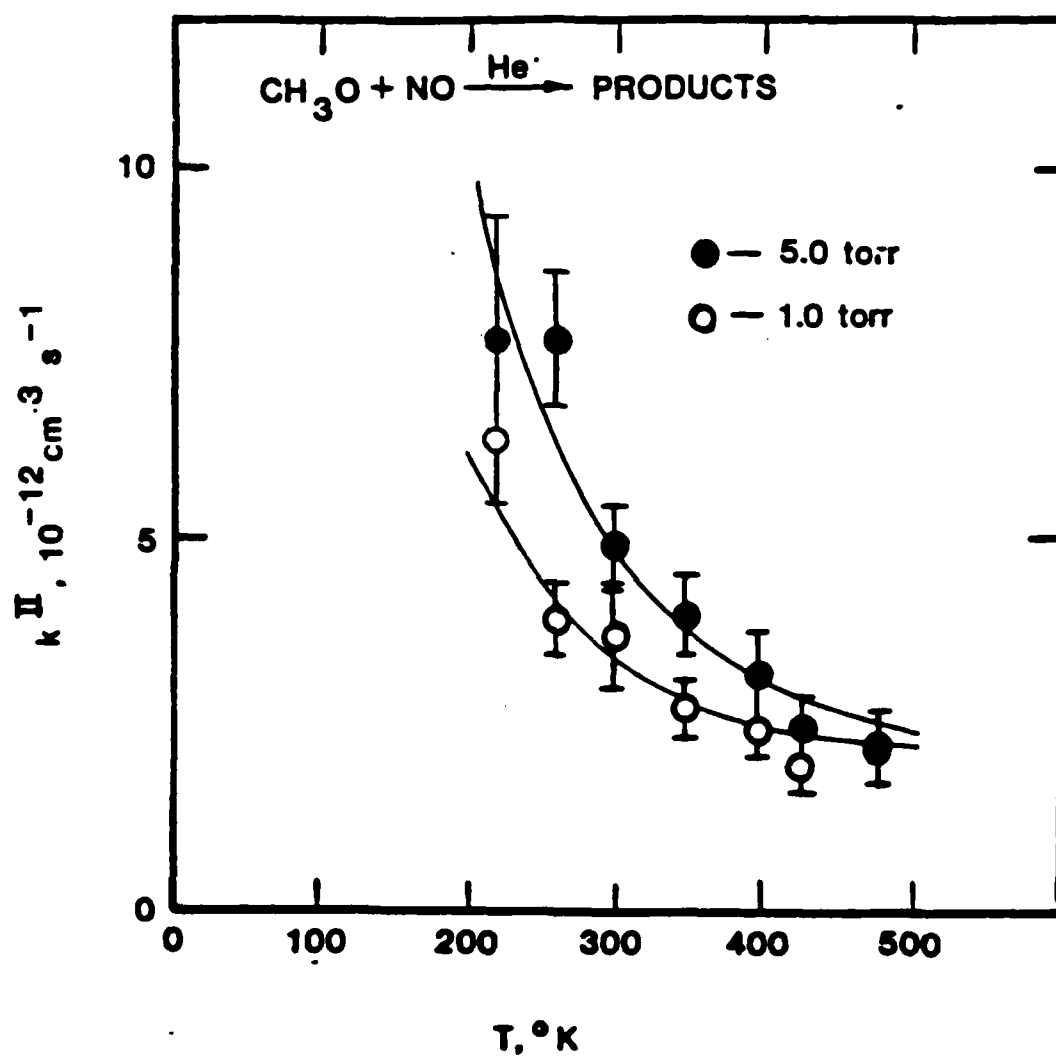


Figure 3 $\text{CH}_3\text{O} + \text{NO}$: pressure and temperature dependence of k_{II}

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Frederick Kaufman

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Michael F. Golde

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